TITLE OF THE INVENTION

SPECTROPHOTOMETER

BACKGROUND OF THE INVENTION

5   [0001]

       The present invention relates to a spectrophotometer.

       [0002]

       Twin-beam spectrophotometers evaluate a sample in
terms of spectral transmittance, spectral reflectance,
10   and other optical characteristics, by splitting the beam
emitted from a light source into a sample beam and a
reference beam and using the ratio of the sample beam
signal S and reference beam signal R obtained by
converting photodetector output signals by use of an
15   amplifier and an A/D converter.

       [0003]

       During wavelength spectral measurement using such a
spectrophotometer, changes in wavelength, λ, change the
levels of signals S and R according to the particular
20   geometric value of $E(\lambda).M(\lambda).D(\lambda)$ which consists of values
such as the energy, $E(\lambda)$, of the light source, the
efficiency, $M(\lambda)$, of the optical system, and the
sensitivity, $D(\lambda)$, of the photodetector. The accuracy of
the data measurements obtained from digital signals
25   depends on the number of digits in the particular digital
signal, and the rate of change due to wavelength is, for
example, in visible and ultraviolet radiation regions,
several tens to several hundreds of times as great. Thus,

in the wavelength regions that the detection system
cannot attain high sensitivity, the accuracy of the
signal ratio with respect to the wavelengths at which the
detection system can attain high sensitivity decreases to
several tenths to several hundredths of times as great.
Accordingly, measurement accuracy significantly decreases
in low-sensitivity wavelength regions.

[0004]

A means effective for avoiding such decreases in
measurement accuracy according to the particular
wavelength of the signal values is by adopting the so-
called "differential feedback" method, in which, each
time data is acquired, the signal threshold value that
establishes the condition of Atar=(Amax+Amin)/2 ... where
A is signal R or S, whichever is the greater in level ...
is to be assigned and when A ≤ Amin or Amax ≤ A, the
sensitivity of the photodetector is to be adjusted so
that signal A always satisfies Amin ≤ A ≤ Amax. By
providing such adjustment each time a data acquisition
operation is to be performed, it is possible to obtain
almost equal signal accuracy at all times, irrespective
of the differences in sensitivity according to wavelength
region.

[0005]

Photomultipliers (also referred to as photomultiplier
tubes) are most commonly used as the photodetectors for
measurement in visible and ultraviolet radiation regions,
and since the sensitivities of photomultipliers change

according to the value of the voltage applied between the cathode and anode of the photomultiplier, its detection sensitivity can be adjusted by varying the value of the voltage to be applied. Output signals from the

5   photomultiplier, however, vary with the product of the sixth to tenth power of (incident light intensity + applied voltage), and thus in a high-sensitivity wavelength region and in a low-sensitivity wavelength region, even if exactly the same correction voltage is

10   applied, a difference in the magnitude of the signal value adjusted will arise from the difference in the original applied voltage. In the photomultiplier, although the magnitude of the output current is taken out as a signal level, if the output current increases too

15   excessively, the output current itself will saturate and the resulting disturbance in the proportionality mentioned above will reduce measurement accuracy. For this reason, Atar is set to the vicinity of the upper limit of the range in which the output current from the

20   photomultiplier does not saturate. In such a case, in order to avoid output saturation associated with voltage correction, the voltage to be applied when one voltage correction operation is to be performed is set to a relatively small value with a high-sensitivity wavelength

25   as its reference.

[0006]

In this method, Amin ≤ A ≤ Amax always holds when variations in wavelength with each data acquisition

operation are sufficiently small in comparison to changes in sensitivity. However, when spectral measurement that requires high-speed wavelength shifting (changes the wavelength at high speed) takes place, changes in the

5 sensitivity of the detection system due to changes in wavelength will increase according to the particular variation in data acquisition wavelength. The consequent decrease in the relative voltage correction value with respect to the particular change in detector sensitivity

10 will reduce the number of digits in the digital signal value (Amin >> A) or saturate the output current of the photomultiplier (A >> Amax), thus resulting in equal measurement accuracy not being obtainable in the entire measuring wavelength region.

15 [0007]

Since a wavelength region in which detection systems can attain high sensitivity must be selected as the basis for specifying the voltage correction value, the occurrence of the problem described above has been

20 particularly significant in the wavelength regions that detection systems cannot attain high sensitivity.

[0008]

Although this problem can be solved by conducting measurements at reduced wavelength shifting speeds, when

25 a multitude of samples are to be measured or when the measuring wavelength range is too wide, reduction in the wavelength shifting speed takes a greater deal of time to perform one measuring operation. When a multitude of

samples are to be measured, therefore, it takes a great deal of time to measure all samples accurately.

[0009]

One method of solving the problem involved is by calculating the voltage correction value from the present voltage value by use of a function, as described in Japanese Application Patent Laid-Open Publication No. Hei-72037 (1993). According to this method, the voltage signal correction value calculated from the present voltage value will be incorporated during next data acquisition. When the wavelength shifting speed is increased, the difference, $|(\lambda 0-\lambda 1)|$, between the present wavelength, $\lambda 0$, and the next data acquisition wavelength, $\lambda 1$, will also increase in proportion to the speed. Therefore, this method poses the new problem that during spectral measurement in the wavelength band where the detection system abruptly changes in sensitivity, the amount of correction does not keep up with any changes in signal level or the amount of correction increases too significantly in itself.

[0010]

During wavelength spectral measurement, the measuring wavelength will shift in one direction each time data is acquired. However, with the correction method where the voltage value for the previous data acquisition is to be incorporated into the present voltage value, accurate sensitivity correction is not possible.

[0011]

To maintain constant spectral measurement accuracy, it is necessary that sample beam signal S or reference beam signal R, whichever is the greater in level, should be taken as signal A and that a signal value within a fixed range should always be obtained as the value of signal A. In order to achieve this, the voltage to be applied to the photomultiplier is controlled to provide differential feedback correction so that the value of signal A always stays within a fixed range. With the prior correction method, however, the energy of the light source, the optical system, and the wavelength characteristics at the sensitivity of the photodetector do not permit constant detector output to be maintained when the measurements that require high-speed wavelength shifting (changing) are conducted, because the relative amount of correction with respect to a change in sensitivity will decrease, especially in the wavelength regions that the sensitivity of the detection system is low. The appearance of such a problem has been significant, especially in the wavelength regions that detection systems cannot attain high sensitivity.

[0012]

Although such a problem can be solved by reducing the wavelength shifting speed, when the measuring wavelength range is too wide, reduction in the wavelength shifting speed takes too much time to perform measurements.

[0013]

This problem also applies to a single-beam

spectrophotometer that uses a single beam to perform

spectral measurements.

SUMMARY OF THE INVENTION

[0014]

It is the object of the present invention to supply a

spectrophotometer that can perform spectral measurements

within a short time and with high accuracy.

[0015]

The present invention is to minimize any influences

of changes in detection system sensitivity and obtain

higher signal accuracy, even during the measurement

process that requires high-speed wavelength shifting,

first by, prior to measurement of a sample, measuring and

storing into a table the voltage value to be used for

controlling the sensitivity of the photodetector, and

then by, during measurement of the sample, providing

sensitivity correction control using the stored voltage

value.

[0016]

More specifically, as outlined in Claim 1, the

present invention is to supply a spectrophotometer having

a light source for emitting an optical beam,

a photodetector that changes in sensitivity with

changes in applied voltage,

an analog-to-digital converter by which electrical

signals from said photodetector are converted into

digital signals,

a digital storage means for storage of said digital signals corresponding to the light of said beam, and

a sensitivity control means for controlling the sensitivity of said photodetector so that the signal values of said digital signals stay within a predetermined range,

wherein the spectrophotometer is characterized in that said sensitivity control means is further equipped with a sensitivity correction data storage means by which sensitivity correction data for adjusting the sensitivity of said photodetector is stored for each wavelength, and a sensitivity correction means for adjusting the sensitivity of said photodetector by applying the sensitivity correction data stored into said sensitivity correction data storage means.

[0017]

Also, as outlined in Claim 2, the present invention is to supply a spectrophotometer having

a light source for emitting an optical beam,

a beam splitting means by which the beam that has been emitted from said light source is split into two beams,

a photodetector that changes in sensitivity with changes in applied voltage,

an analog-to-digital converter by which electrical signals from said photodetector are converted into digital signals,

a digital storage means for storage of said digital

signals corresponding to the light of said two beams,

a sensitivity control means for controlling the sensitivity of said photodetector so that the signal values of said digital signals stay within a

5 predetermined range, and

a calculation means for calculating the ratio of the digital signals corresponding to the two beams stored into said digital storage means,

wherein the spectrophotometer is characterized in

10 that said sensitivity control means is further equipped with a sensitivity correction data storage means by which sensitivity correction data for adjusting the sensitivity of said photodetector is stored for each wavelength, and a sensitivity correction means for adjusting the

15 sensitivity of said photodetector by applying the sensitivity correction data stored into said sensitivity correction data storage means.

[0018]

Also, as outlined in Claim 3, said sensitivity

20 control means is characterized in that it stores into said sensitivity correction data storage means the sensitivity correction data corresponding to measuring wavelength bands, and during the measurement of a sample, adjusts the sensitivity of said photodetector by applying

25 the sensitivity correction data stored within said sensitivity correction data storage means.

[0019]

Also, as outlined in Claim 4, said sensitivity

control means is characterized in that it provides said
photodetector with sensitivity correction control in
order for the beam signal of the photodetector to stay
within a predetermined range during the measurement of a
sample that changes wavelength at high speed.

[0020]

Also, as outlined in Claim 5, said sensitivity
control means is characterized in that it provides said
photodetector with sensitivity correction control in
order for one of the two beam signals of the
photodetector to stay within a predetermined range during
the measurement of a sample that changes wavelength at
high speed.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a functional block diagram of an
ultraviolet/visible region spectrophotometer, an
embodiment of the present invention.

Fig. 2 is a flowchart of the control process that the
control unit of the ultraviolet/visible region
spectrophotometer shown in Fig. 1 autonomously performs
or gets the data-processing unit to perform.

Fig. 3 is a diagram showing the relationship between
the voltage data storage table of the ultraviolet/visible
region spectrophotometer shown in Fig. 1, and the applied
voltage value existing during measurement of the sample.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0021]

Embodiments of the present invention are described in detail below taking as an example a twin-beam spectrophotometer which has a wavelength spectral measuring capability.

[0022]

Fig. 1 is a functional block diagram of an ultraviolet/visible region spectrophotometer, an embodiment of the present invention. The light source consists of a combination of an WI lamp 1, which emits light of a visible region, and a D2 lamp 2, which emits light of an ultraviolet region. The beam that has been emitted from the light source is reflected by a light source selection mirror 3 and then enters a first spectroscope 5 through a rotating shutter 4.

[0023]

First spectroscope 5 receives light via a split 6, and the light enters a prism 9 via mirrors 7 and 8. Prism 9 splits the incident light into beams and emits the beams towards said mirror 8. After receiving the split beams from prism 9, mirrors 8 and 9 transfer the beams to a second spectroscope 11.

[0024]

Second spectroscope 11 receives the incident beams via a mirror 12, a slit 13, and a mirror 14, and transfers the beams to a diffraction grating 15. After splitting the incident beams, diffraction grating 15 emits the beams via a mirror 16, a slit 17, and a mirror

18.

[0025]

After receiving the beams from second spectroscope 11,
mirrors 19 and 20 transfer the beams to a rotating

5   spectral mirror 21, where the beams are then branched
into two optical paths. The reference beam, which is one
of the beams, enters a samples room 24 via mirrors 22 and
23, and after the beam has been reflected directly
towards a photodetector 26 by a mirror 25. The sample

10   beam, which is the other beam, enters samples room 24 via
mirror 7, and then enters said photodetector 26 via the
sample (not shown in the figure). A photomultiplier is
used as photodetector 26.

[0026]

15   Under the control of control unit 32, data-processing
unit 31 receives a detection signal from said
photodetector 26 and processes the signal.

[0027]

Control unit 32 has a control processing program and

20   a voltage data storage table, which is a sensitivity
correction data storage means, and performs a control
process comprising steps of controlling the driving
motors (not shown in the figure) that drive said data-
processing unit 31, light source selection mirror 3,

25   rotating shutter 4, prism 9, and rotating spectral mirror
21 in accordance with entered instructions from an input
unit 33, controlling the applied voltage of photodetector
26, and displaying samples measuring conditions and

measurement results on a display unit 34.

[0028]

Data-processing unit 31, control unit 32, input unit
33, and display unit 34 are components of a compact
(personal) computer system, and each unit contains a RAM.

[0029]

Next, the control process 31 performed by said
control unit 32 is described below. Fig. 2 is a flowchart
of the control process that the control unit 32 itself
performs or gets data-processing unit 31 to perform. Fig.
3 shows the relationship between the voltage data storage
table and the applied voltage value existing during
measurement of the sample.

[0030]

First, the processing sequence relating to voltage
data storage and measurement is described below.

[0031]

Step 101

Conditions for storing and measuring the voltage
value to be used to control photodetector 26 are entered
in accordance with the instructions of input unit 33.

[0032]

Step 102

The voltage data storage and measurement process is
started, subject to the corresponding instruction.

[0033]

Step 103

The wavelength driving motor for changing the

measuring wavelength is controlled to move prism 9 and diffraction grating 15 to the starting wavelength of measurement.

[0034]

Step 104

The output signal from photodetector 26 is amplified and A/D converted to obtain a sample beam signal S and a reference beam signal R.

[0035]

Step 105

The correction voltage value is determined from the signal values that were obtained in step 104 above.

[0036]

Step 106

A voltage based on the correction voltage value that was determined in step 105 above is applied to photodetector 26.

[0037]

Step 107

The present voltage value is saved in the present wavelength position of a voltage data storage table 301.

[0038]

Step 108

The wavelength driving motor is controlled so as to achieve shifting to the next measuring wavelength. The wavelength shifting interval in this case provides the basis for shifting the next sample-measuring wavelength and must therefore be set to a sufficiently short value

so that the sensitivity of the detection system changes too significantly. The sensitivity of the detection system undergoes characteristic changes according to the particular design specifications of the apparatus, such as the energy of the light source, the efficiency of the optical system, and the sensitivity characteristics of the photodetector. It is therefore advisable to provide independent limits for each apparatus component so that the wavelength shifting speed for storing and measuring the voltage value can be selected only from a fixed range.

[0039]

Step 109

It is judged whether the ending wavelength within the required measuring range has been exceeded, and if the measuring wavelength is not in excess of the ending wavelength, control will be returned to step 104 and the measurement will be repeated. When the ending wavelength is exceeded, control will proceed to the next step, 110.

[0040]

Step 110

The voltage data storage and measurement process is terminated.

[0041]

Next, the processing sequence relating to measurement of a sample is described below. This sequence is executed, only when a sample is mounted at the sample beam side of the samples room and voltage data is present in voltage data storage table 301.

[0042]

Step 201

Sample-measuring conditions are entered from input unit 33. When the instruction to use a stored voltage value is entered, if no voltage data is present in voltage data storage table 301, a warning message will be displayed on display unit 34.

[0043]

Step 202

The sample-measuring process is started, subject to the corresponding instruction.

[0044]

Step 203

The wavelength driving motor is controlled to move prism 9 and diffraction grating 15.

[0045]

Step 204

As shown in Fig. 3, the voltage value corresponding to the present wavelength position in voltage data storage table is read out and applied to photodetector 26. The voltage at the present wavelength position in this case becomes the optimum voltage value for the present wavelength position which has been obtained during voltage data storage and measurement beforehand. Even when high-speed wavelength shifting is selected, therefore, the appropriate voltage can be applied to photodetector 26 and thus the insufficiency in the number of digits in the signal value, the saturation of output,

or other problems do not occur.

[0046]

Step 205

The output signal from photodetector 26 is amplified and A/D converted to obtain a sample beam signal S and a reference beam signal R and then to calculate the data ratio between signals S and R.

[0047]

Step 206

The value that was calculated in step 205 above is saved in a voltage data storage table 302.

[0048]

Step 207

The wavelength driving motor is controlled so as to achieve shifting to the next measuring wavelength.

[0049]

Step 208

It is judged whether the ending wavelength within the required measuring range has been exceeded, and if the measuring wavelength is not in excess of the ending wavelength, control will be returned to step 204 and the measurement will be repeated. When the ending wavelength is exceeded, control will proceed to the next step, 209.

[0050]

Step 209

The sample-measuring process is terminated.

[0051]

[Effects of the Invention]

According to the present invention, since the voltage value for controlling the sensitivity of the photodetector is measured and stored into a table prior to measurement of a sample, and since sensitivity correction control using the stored voltage value is provided during measurement of the sample, even when the measurement process that requires high-speed wavelength shifting is performed, any influences of changes in detection system sensitivity can be minimized and higher signal accuracy can be obtained.